

SYMPOSIUM ON CHARACTERIZATION AND CHEMISTRY OF OIL SHALES  
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ELECTRON PARAMAGNETIC RESONANCE AND THERMOGRAVIMETRIC INVESTIGATIONS OF  
THE PYROLYSIS OF EASTERN SHALES

By

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INTRODUCTION

The organic matter in oil shale is composed mostly of kerogen (insoluble in common organic solvents) with a few percent soluble bitumen. When Green River oil shale is heated to 573 K, natural bitumen can be removed thermally from oil shale. The chromatogram of thermally separated bitumen is identical to that of the solvent-extracted bitumen (1). At temperatures above 573 K, the kerogen decomposes to bitumen and subsequently bitumen to oil and gas (2, 3). While considerable work has been done using Electron Paramagnetic Resonance (EPR) on coal (4, 5) and western oil shale (6, 7), relatively little is known about eastern shales. EPR measurements yield direct, in situ information on the kinetics of the organic-free radicals present in heated shale and natural bitumen. The present work was undertaken as a correlated EPR and TGA investigation of eastern shales to elucidate the pyrolysis mechanisms of these shales.

EXPERIMENTAL

Oil shale samples used in the present study are Kentucky Sunbury oil shale and Tennessee U. S. oil shale. Chemical analyses of the oil shales are given in Table I.

TABLE I  
CHEMICAL PROPERTIES OF OIL SHALES

Type of Oil Shale/ Analysis Items, Wt %	Sunbury Oil Shale Kentucky	U. S. Oil Shale Tennessee
Hydrogen	1.55	1.31
Nitrogen	0.53	0.36
Total carbon	14.07	11.49
Oxygen (by difference)	3.30	0.04
Silicon, SiO <sub>2</sub>	66.70	60.74
Aluminum, Al <sub>2</sub> O <sub>3</sub>	20.00	13.76
Iron, Fe <sub>2</sub> O <sub>3</sub>	7.80	15.30
Calcium, CaO	0.20	8.47
Magnesium, MgO	1.40	1.52
Sodium, Na <sub>2</sub> O	1.14	0.67
Potassium, K <sub>2</sub> O	5.10	4.91
Phosphorus, P <sub>2</sub> O <sub>5</sub>	0.24	0.17
Titanium, TiO <sub>2</sub>	0.72	0.88
Sulfur, SO <sub>3</sub>	0.52	1.01

EPR measurements were made with a Brüker-IBM EPR spectrometer Model ER 200D fitted with an NMR gaussmeter and a digital frequency counter for measuring the microwave frequency. The peak-to-peak line widths,  $\Delta H_{pp}$ , were measured by using a Brüker NMR gaussmeter. The data acquisition and reduction was carried out with a Brüker Model Aspects 2000 computer. The in situ, high-temperature EPR measurements were made with a Brüker high-temperature cavity Model 4114 HT. The g-values and the line widths,  $\Delta H_{pp}$ , were measured by the least squares fitting of the observed signals using the Aspects 2000 computer.

The oil shale sample was heated at  $\sim 8\text{K/min.}$  in  $40^\circ$  intervals, the temperature was stabilized for  $\sim 15$  minutes, and then the EPR spectrum was recorded. The sample temperature was measured with a chromel-alumel thermocouple located close to the sample. The temperature stability was  $< 1\text{K}$  over a 20-minute period.

The TGA experiments were carried out by a DuPont 951 thermogravimetric balance interfaced with a DuPont 1090 thermal analyzer. Details of the TGA measurements are given elsewhere (8).

## RESULTS AND DISCUSSION

Figure 1 shows typical TG and DTG curves for Kentucky Sunbury shale (8). There are two major peaks from the derivative weight loss/temperature curve. The first peak begins about  $20^\circ\text{C}$  and ends about  $100^\circ\text{C}$  while the second peak begins about  $350^\circ\text{C}$  and ends about  $550^\circ\text{C}$ . It is likely that the first peak represents the volatilization of water, while the second peak represents the decomposition of pyrolytic bitumen. The differential weight variation between two peaks is considered to be the decomposition of natural bitumen and kerogen.

Figure 2 shows typical EPR scans for the two samples: (a) for the Sunbury oil shale and (b) for the U. S. oil shale. Both spectra consists mainly of some broad signals covering a range of about 1000 G over which are superimposed sharp lines from organic-free radicals (indicated with arrowheads) at g-values around  $2.006 \pm 0.001$ . It may be noted that the broad signals, attributable to  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  or related impurity, are more abundant in the U. S. shale than the Sunbury oil shale.

Figures 3 and 4, respectively, show the measured temperature dependence of the free radical concentration (c) as measured by the area under the signal corrected by the high-temperature Curie-Weiss behavior, the peak-to-peak line widths ( $\Delta H_{pp}$ ) in Gauss and the line positions (g-values). Figure 3 is for the U. S. oil shale and Figure 4 shows similar results for the Sunbury oil shale. In both cases, part (a) shows temperature dependence of the g-values, and (b) and (c) are those of the peak-to-peak line width ( $\Delta H_{pp}$ ) for the free radical EPR signal and the free radical concentrations, respectively. It is seen that, in both cases, the free radical concentration is fairly constant up to about 300K and then rises steeply, especially around  $600 \pm 10\text{K}$ . A close correlation between the sharp increase in free radical concentration for the Sunbury shale shown in Figure 4 with the maximum in the DTG curve for Sunbury shale in Figure 1. For the U. S. oil shale, there are two somewhat unresolved peaks. For the Sunbury shale, a peak and a shoulder are also visible in about the same temperature range, but here the peak resolution is even less.

The peak-to-peak line width,  $\Delta H_{pp}$ , of the EPR derivative signals from the two shales showed strikingly different temperature dependence. With the increase in temperature, the line width of the U. S. shale is fairly constant up to about 600 K, exhibits a sharp increase around 620 K and then drops sharply to about 60% of the maximum value at about 800 K. It is noted that the minimum line width occurs at about the same temperatures as that corresponding to the maximum in the free radical concentration.

The peak-to-peak line width ( $\Delta H_{pp}$ ) for the Sunbury shale shows a steady decrease from about 200 K to a minimum at about 560 K and then increases to about the original value at about 800 K, the maximum temperature in our measurements on this shale. We found that, for this shale, an excessive microwave loss in the cavity due to some change in the shale prevented us from EPR measurements at higher temperature (the mechanism for this microwave loss is unclear but experiments are in progress). Once again, the minimum in the  $\Delta H_{pp}$  occurs at about the temperature of the start of the smaller peak in the free radical concentration. However, the excessive microwave loss for this sample might be the cause of the broadening of  $\Delta H_{pp}$  above 600 K.

The g-values of both samples exhibit a fairly small ( $< 0.1\%$ ) but steady increase with temperature. The broad maxima in the g-value plots occur roughly at the temperature of the maxima in the free radical concentration for both shales.

The results of Figures 3 and 4 clearly demonstrate that the free radical concentration changes by nearly one order of magnitude for both shales as the results of pyrolysis. It is clear that the line widths ( $\Delta H_{pp}$ ) also change drastically as a result of the heating, indicating that pyrolysis results in probably new types of free radicals, different from those already present in the shale sample. This conclusion is supported by plot (a) wherein the g-values also exhibit a definite slowly increasing trend with temperature increase.

Sample: KENTUCKY SHALE  
 Size: 59.96 mg  
 Rate: 10 DEG/MIN 100CC N2/MIN

# TGA

Date: 6-Oct-83 Time: 22:45:45  
 File: SUNBURY.07  
 Operator: M. SHEN

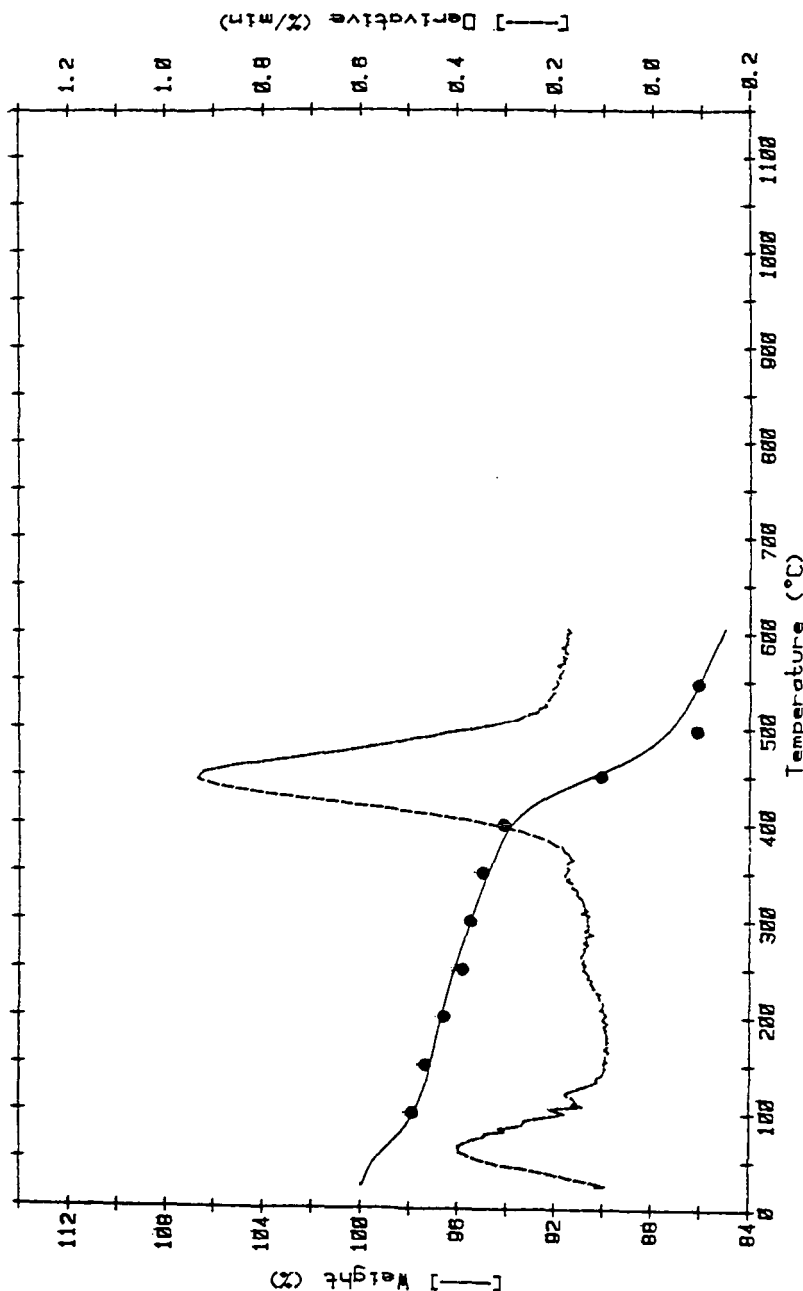


Figure 1. Typical TG and DTG curves for Kentucky's Sunbury oil shale.

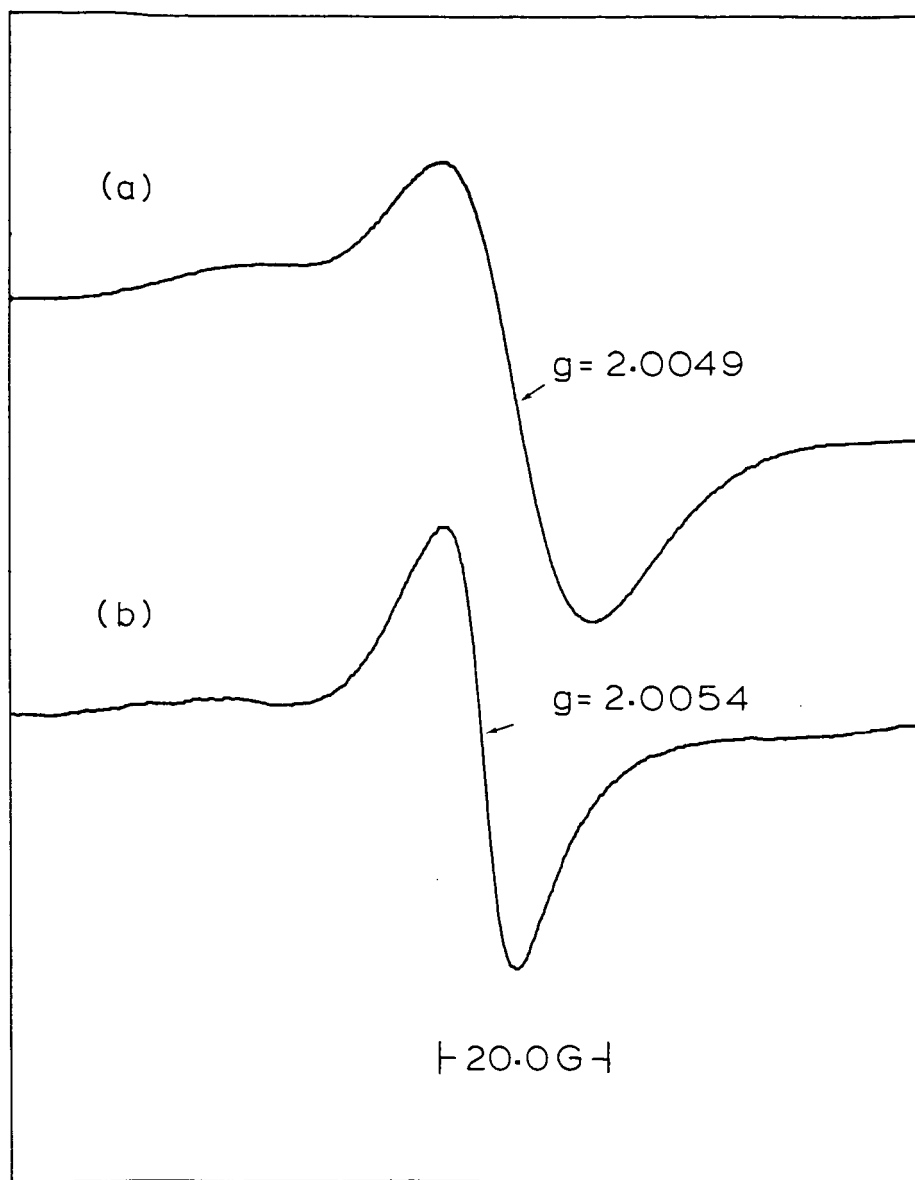


Figure 2. Typical EPR spectra of (a) Kentucky's Sunbury oil shale and (b) Tennessee's U. S. oil shale.

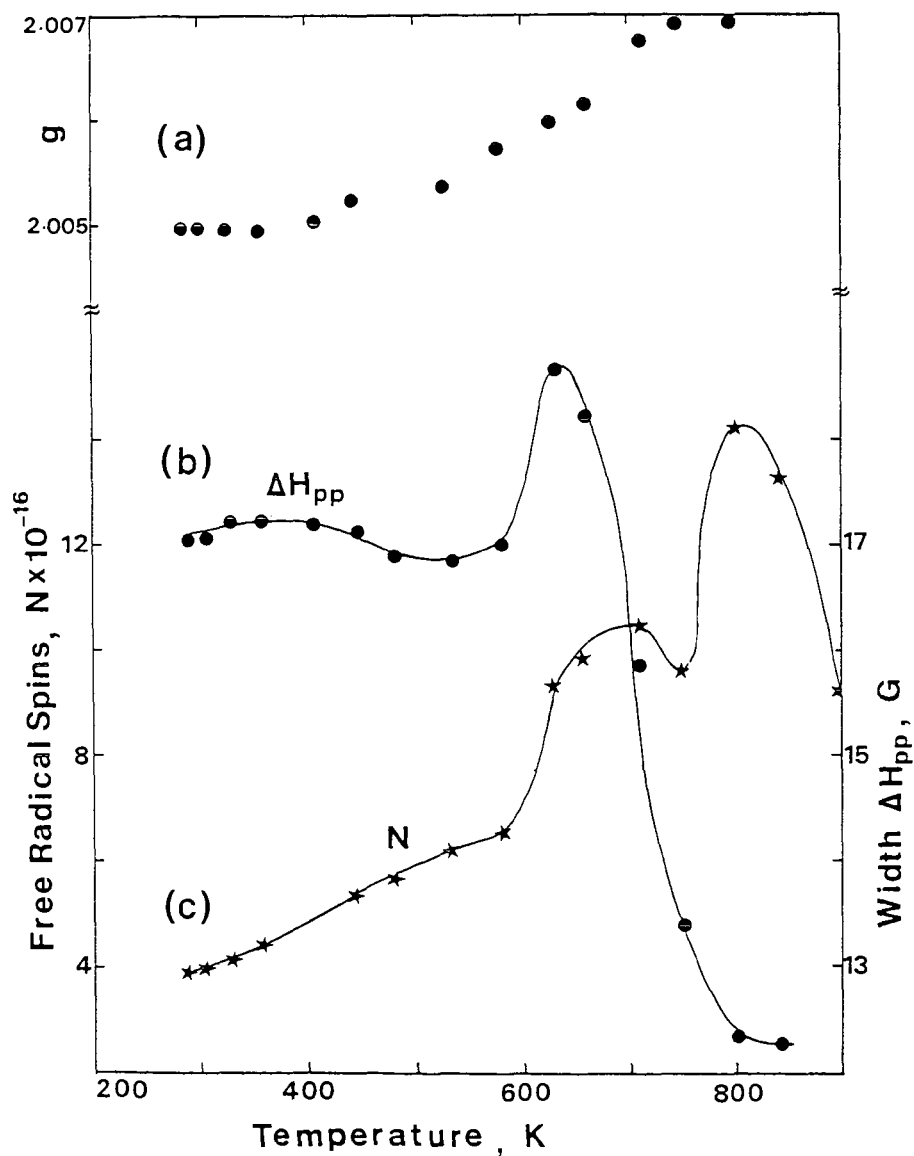


Figure 3. Temperature dependence of the EPR parameters for Tennessee's U. S. oil shale: (a) G-values, (b) peak-to-peak line widths and (c) concentration of the radicals relative to room temperature.

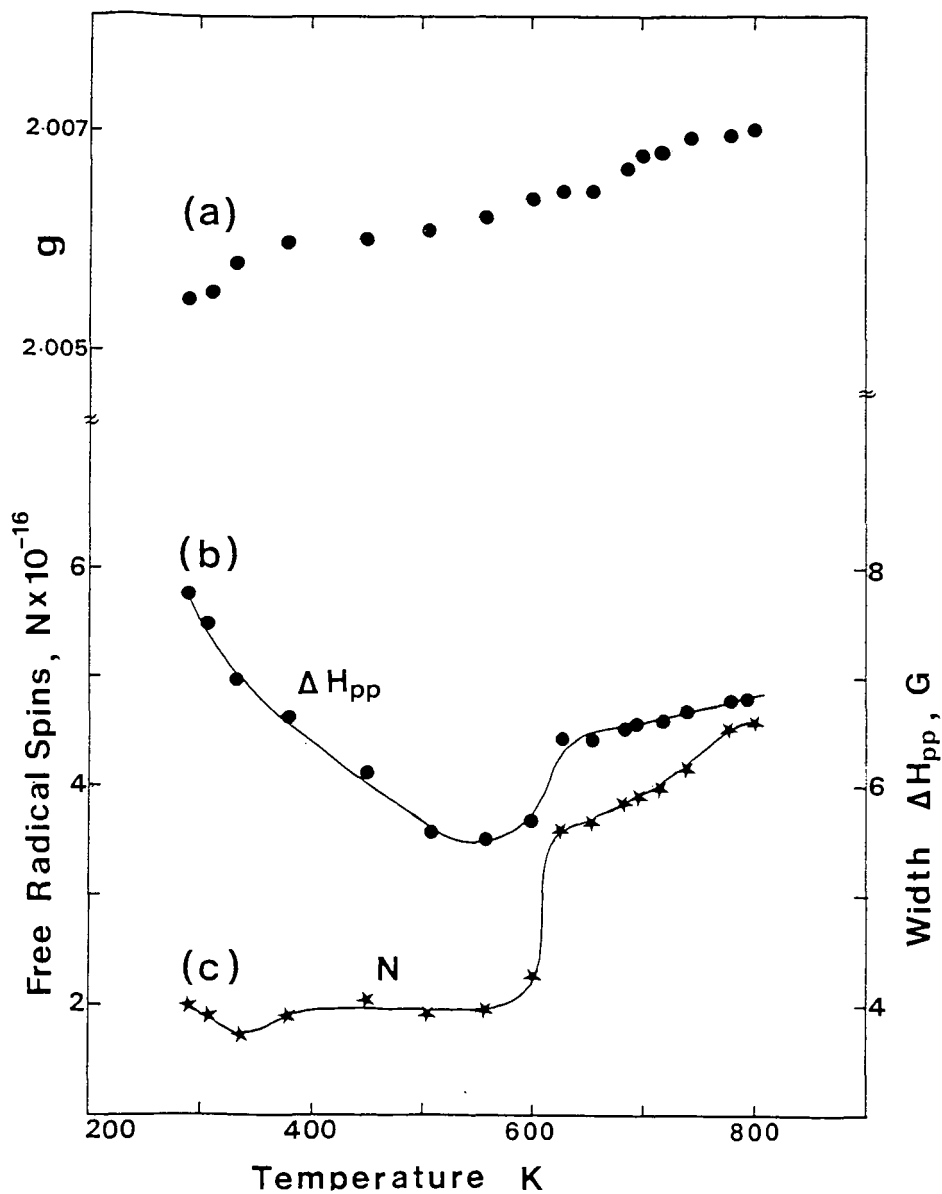


Figure 4. Temperature dependence of the EPR parameters for Kentucky's Sunbury oil shale: (a) g-values, (b) peak-to-peak line widths and (c) relative concentration.

We note that the decrease in  $\Delta H_{pp}$  concomitant with the increase in the free radical intensity might also be interpreted simply as a result of spin exchange narrowing, as is well known to happen for concentrated spin systems. However, the comparison with  $g$ -values suggests that the linewidth change is perhaps more likely to be due to the formation of new species of radicals.

As far as the identification of the radicals is concerned, it is clear from the  $g$ -values (being close to the free electron  $g$ -value of 2.0023) that the radicals are all fairly similar in nature. Comparison with the pyrolysis results of Retcofsky et al. on coal samples suggests that the radicals are essentially  $\pi$ -type delocalized hydrocarbon radicals. The increase of the  $g$ -value over 2.0023 shows that the free electron resides also partly on heteroatoms with spin-orbit coupling larger than carbon, possibly oxygen, sulfur or nitrogen.

Figures 3 and 4 show that the  $g$ -values of the two shale samples are nearly the same (2.007) at the high temperature end. The significant positive deviation from the free electron value of 2.0023 suggests that the free radicals in both shales are essentially of the same nature; the deviation being largely due to the spin-orbit coupling of a heteroatom in the free radical structure. However, the data on chemical analysis (Table I) show that nitrogen and oxygen are significantly larger in Sunbury oil shale than in the U. S. oil shale while the sulfur is larger in the U. S. oil shale. Since sulfur has much larger spin-orbit coupling constant than oxygen or nitrogen, the presence of sulfur in a radical will cause its  $g$ -value to be much higher than that for a similar radical containing oxygen or nitrogen. The present EPR data show that the  $g$ -values for both samples are nearly the same. Thus, these results indicate that the newly formed free radicals in the U. S. oil shale are preferentially formed around the sulfur moiety.

Another interpretation of the line width decrease at high temperature is that the decrease results from the loss of hydrogens on pyrolysis, as found for coal samples. This interpretation implies that the original cause of the EPR line width is the dipolar coupling between the unpaired electron of the free radical and the protons from the C-H hydrogens. However, there is no direct proof for this hypothesis. We plan to carry out electron-nuclear double resonance (ENDOR) studies to clarify the origin of the line widths and to identify the structures of the produced organic radicals.

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